

PHOSPHATE (U-Th)/He THERMOCHRONOLOGY OF APOLLO 14 MELT BRECCIA 14311. C. A. Diaz¹, R. M. Flowers¹, C. A. Crow¹, J. R. Metcalf¹, R. Economos², T. Erickson^{3,4}, J.W. Boyce⁴, J. Davis¹, M. Brounce⁴, K. Lehman-Franco², B. Schoene⁵ ¹Department of Geological Sciences, University of Colorado at Boulder, Boulder, CO 80309, ²Department of Earth Sciences, Southern Methodist University, Dallas, TX 75275, ³Jacobs-JETS, ⁴NASA Johnson Space Center, Houston, TX 77058, ⁴Earth & Planetary Sciences, University of California, Riverside, CA 92521. ⁵ Department of Geosciences, Princeton University, Princeton, NJ 08544. Email:connor.diaz@colorado.edu.

Introduction: Our ability to confidently characterize the impact history of the inner solar system is limited by discrepancies in radiometric dates and age interpretations for lunar rocks, impact melts, and recovered meteorites. It is therefore important to explore different thermally sensitive radiometric systems to unravel the timing and extent of the long-term impact flux. Low-temperature thermochronology of lunar samples has the potential to provide more complementary geochronological datasets and further test dynamical models related to the evolution of the inner solar system (e.g., [1]).

(U-Th)/He dating is based on the production of ⁴He atoms by radioactive alpha decay of U and Th (and to a lesser extent, Sm) in a crystal and the thermally activated volumetric diffusion of those ⁴He nuclides. At high temperatures, the crystal is an open system from which ⁴He can escape; at lower temperatures, ⁴He may be retained. This retention temperature depends on factors such as crystal structure and volume fraction of radiation damage in the crystal (e.g., [2, 3]), but is significantly lower for phosphate minerals compared to the diffusion of the radiogenic daughter products in other widely used chronometric systems (e.g., ~75°C in terrestrial apatite (U-Th)/He vs. ~500°C in apatite U-Th-Pb vs. ~900°C in zircon U-Th-Pb chronometry). Phosphate (U-Th)/He dating has been used to decipher peak temperatures and cooling rates related to terrestrial impact events (e.g., [4]). Pairing a low-temperature thermochronometer with higher-temperature approaches (i.e., a combined ²⁰⁷Pb-²⁰⁶Pb and (U-Th)/He approach), can therefore resolve multiple impact ages within a given sample or even grain. However, despite its potential, phosphate (U-Th)/He dating has not been reported on any lunar samples. Here we present the first lunar phosphate (U-Th)/He thermochronology on an Apollo 14 impact melt-breccia.

Sample Context: Lunar impact melt-breccia sample 14311 was collected at station Dg [5], at the boundary of the continuous ejecta blanket of Cone Crater [6], a small (340 m wide, 75 m deep) crater suggested to have formed ca. 25-40 Ma [7]. Exposure age estimates for sample 14311 range from ca. 528 [8] to 661 Ma [9]. These estimates contrast greatly with near-surface cosmic-ray exposure ages from other breccia samples from Apollo 14, which range from ca.

25 Ma to 379 Ma (e.g., [8, 9]). The unique residence time of 14311 has fueled speculation that it originated from a different location than other surrounding breccias.

The Apollo 14 landing site is covered by a heterogeneous ejecta blanket from the Imbrium impact (ca. 3.85-3.95 Ga), called the Fra Mauro Formation. This landing site was chosen based on its proximity to the Cone Crater, which is thought to have penetrated through the surface regolith and excavated part of the Fra Mauro Formation (e.g., [5]). The breccia samples collected at the Apollo 14 landing sites could represent different excavation depths within the Fra Mauro Formation. Therefore, each breccia could have experienced a distinct cooling history owing to spatially heterogeneous impact effects and/or Cone Crater excavation [10]. Additional geochronologic investigation is needed to further constrain the history of Apollo 14 breccia materials.

Sample Description: Sample 14311 is a melt-poor, polymict impact-melt breccia of >75% crystalline-matrix (formed by a pyroxene and plagioclase mosaic), and 5-25% mineral (pyroxene, plagioclase, Fe-Ti oxides) and lithic clasts of igneous rocks and breccias [5, 11, 12]. This breccia is interpreted to be a mix of pre-Imbrium crust and Imbrium impact melt (e.g., [11]). The crystalline matrix has a low abundance of quenched impact melt and is dominated by an “equant texture” (lacks glass, while silicate and oxides form a mosaic pattern). This texture is indicative of solid-state recrystallization of ejecta material at temperatures >1000°C [10, 13]. It is the only crystalline-matrix breccia collected near Cone crater [8, 14]. Sample 14311 was chosen due to its high phosphorus content and context provided by previous zircon (U-Th)/He (ZHe) study of this same sample [15].

Approach: Recent ZHe analyses of 14311 showed a negative ZHe date-eU correlation (a proxy for radiation damage from alpha decay) that spanned from >3500 Ma to ~110 Ma [15]. Our combined phosphate ²⁰⁷Pb-²⁰⁶Pb and (U-Th)/He study tests this proposed history of impact-related ⁴He loss and radiation damage accumulation to decipher more details of the thermal record of bombardment.

Methods: As part of a larger consortium effort, sample 14311,58 was crushed, sieved, and magnetically

separated. Scanning Electron Microscopy (SEM) mapping and Energy Dispersive Spectroscopy (EDS) spot analyses were used to identify and discriminate between apatite and merrillite. Electron Backscatter Diffraction (EBSD) spot and mapping analyses were done to ensure homogeneity in the crystal lattices. ^{207}Pb - ^{206}Pb analyses were performed on the Cameca ims1290 high-resolution ion microprobe in mono-collection spot mode at the University of California, Los Angeles following the techniques described in [16].

Phosphate shapes and sizes were characterized using the Zeiss Xradia 520 Versa X-ray Microscope (XRM) and Nano/Micro-Computed Tomography System at the University of Colorado Boulder. The reconstructed X-ray data were then processed using “Blob3D” (v2015; [17]), a program that allows for the separation of discrete objects in solid samples to obtain precise volumes for individual phosphate fragments.

Phosphate grains were then carefully extracted from epoxy mounts, placed into Nb tubes, and analyzed on an ASI Alphachron helium measurement line, where degassed ^4He was analyzed on a Balzers PrismaPlus QME 220 quadrupole mass spectrometer. After degassing, phosphates were spiked with a ^{235}U - ^{230}Th - ^{145}Nd tracer, dissolved using a multi-step acid vapor dissolution process, diluted with deionized water, and analyzed for U, Th, and Sm amounts using an Agilent 7900 quadrupole ICP-MS. ^4He amounts were corrected for cosmogenic ^4He produced by galactic cosmic rays using the maximum ^4He production rates from the experiments of [18]. (U-Th)/He dates were then calculated iteratively, both assuming no alpha-ejection correction (an approach adopted for extraterrestrial samples that assumes the dated grains were fragmented during mineral separation or a recent impact event) and correcting for alpha-ejection (assuming all surfaces of the grain were ejection surfaces for an extended interval).

Preliminary Results and Discussion: Both uncorrected and corrected (U-Th)/He dates range from tens of Ma to thousands of Ma. Preliminary results point toward a possible positive phosphate (U-Th)/He date-eU correlation, with older dates lying at high eU (several hundred ppm), decreasing to younger dates at lower eU (single digit ppm). Positive date-eU correlations are common in terrestrial apatite samples affected by protracted thermal histories and extended radiation damage accumulation.

Notably, our corrected (U-Th)/He dates encompass a similar range as the published uncorrected ZHe dates from the same breccia sample [15]. Additionally, multiple phosphate grains preserve corrected (U-Th)/He dates close to their ^{207}Pb - ^{206}Pb crystallization ages around the timing of the Imbrium impact event (~3.9

Ga), illustrating the ability of lunar phosphate to retain ^4He over vast timescales. However, other grains yield (U-Th)/He dates much younger than ^{207}Pb - ^{206}Pb dates, indicating that the (U-Th)/He data contain information about thermal resetting that is not recorded by higher temperature thermochronometers like ^{207}Pb - ^{206}Pb .

Future Work: We plan to continue collecting (U-Th)/He phosphate dates for the remaining 14311,58 grains to better establish the data distribution and potential date correlations with eU and other factors. A series of forward models will be performed using the HeFTy software [19] and the apatite radiation damage model of [20] to calculate the predicted distribution of dates for a range of U-Th compositions and various potential thermal scenarios relating to known impact events. By constraining peak temperatures and cooling durations during multiple impact events through combined microstructure, geochronologic, and modeling efforts, we can therefore potentially test proposed impact histories and decipher the thermal record of bombardment in greater detail.

Acknowledgments: We would like to thank AARB and the NASA Curation Office for access to the samples used in this study.

References: [1] Morbidelli A. et al. (2012) *EPSL*, 355-356, 144-151. [2] Farley, K.A. (2000) *JGR*, 105, 2903-2914. [3] Shuster, D.L. et al. (2006) *EPSL*, 249, 148-161. [4] Ukstins I. A. et al. (2022) *Quaternary Geology*, 67, 10127. [5] Swann G. A. et al. (1977) *USGS Prof. Paper 880*, pp. 103. [6] Stöffler D. (1989) *LPI Technical Report 89-03*, 138-144. [7] Turner G. et al. (1971) *Earth Planet. Sci. Lett.*, 12, 19-35. [8] Stadermann F. J. et al. (1991) *Geochim. Cosmochim. Acta.*, 55, 2339-2349. [9] Crozaz G. et al. (1972) *LPS III*, 2917-2931. [10] Warner J. L. (1972) *LPS III*, 623-643. [11] Simonds C. H. et al. (1977) *LPS VIII*, 1869-1893. [12] Carlson I. C. and Walton W. J. A. (1978) *Johnson Space Center Pub. #14240*. [13] Stöffler D. et al. (1989) *LPI Technical Report 89-03*, 145-148. [14] Drozd R.J. et al. (1977) *LPS VIII*, 3027-3043. [15] Kelly N. M. et al. (2018) *EPSL*, 482, 222-235. [16] Mojzsis S. J. et al. (2014) *Geochim. Cosmochim. Acta.*, 133, 68-96. [17] Ketcham R. A. (2005) *Geosphere*, 1, 32-41. [18] Leya I. et al. (2004) *Meteoritics & Planet. Sci.*, 39, 367-386. [19] Ketcham R. A. (2005) *Reviews Min. Geochem.*, 58, 275-314. [20] Flowers R. M. et al. (2009) *Geochim. Cosmochim. Acta.*, 73, 2347-2365.